fluorescence is observed originating only from Q_y transitions. This suggests that there is extremely efficient coupling between these two states in the monomer, but the observation of Q_x emission in the dimer shows that nonradiative pathways between the Q_x and Q_y levels are less probable in the dimer.

We observe that the radiative lifetime of the Q_x band fluorescence is longer than that of the Q_y emission. This difference is consistent with the suggestion that there is reduction in the number of nonradiative pathways from Q_x in the dimer compared to the monomer.

From a comparison of the corresponding absorption spectra of monomer and dimer of BChl *a* and of Chl *a*, it is noted that the integrated absorptions over the Q_y bands of the monomeric and dimeric species in solution are similar. This is also true for the Q_x absorption bands. If we assume that the direct matrix elements from the ground state to Q_y and to Q_x are of the same order of magnitude,[14] then, from the relative integrated absorption strengths of the two bands, the lifetimes of the two states, $\tau_{abs}^{Q_y}$ and $\tau_{abs}^{Q_x}$, may be shown to be such that $\tau_{abs}^{Q_x} < \tau_{abs}^{Q_y}$. Lifetimes measured for fluorescence are reduced by the existence of nonradiative channels, but the longer lifetime of the Q_x fluorescence band compared with that of the Q_y fluorescence is not inconsistent if nonradiative channels from Q_x are less effective in the dimer. It is not known to what degree triplet states may play a role in these nonradiative processes, but this may be determined from nonlinear absorption studies.[26,27]

The fluorescence yield of monomeric BChl *a* in solution ($\Phi_{fl} \sim 0.2$) is less than that of Chl *a* in solution ($\Phi_{fl} \sim 0.3$).[14] The fluorescence intensities of the dimeric solutions of BChl *a* are observed to be weaker than that of dimeric Chl *a* in solution. This suggests that there are more nonradiative channels for deexcitation of BChl *a* than in Chl *a*; this may be a result of the lowering of the symmetry in BChl *a* relative to Chl *a* by the additional carbonyl group at C_{2a} in BChl *a* which is in conjugation with the π system of the macrocycle.

It is interesting that the dimer and oligomers of Chl *a* exhibit a marked red shift in their absorption and fluorescence maxima with respect to those of the monomer, while the maxima of the fluorescence and absorption spectra of the BChl *a* dimer and oligomers, if shifted at all, show a blue shift. The sensitivity of the shift and bandwidth of dimeric chlorophylls to geometrical structure has been noted for a number of synthetic linked chlorophyll dimers.[28-31] This observation indicates that the detailed structures of the dimers of Chl *a* and BChl *a* may not be identical, although the fluorescence results reported above for the two chlorophyll dimers are analogous in the observation of the activity of the Q_x fluorescence transition.

Registry No. BChl *a* dimer, 18025-10-0; Chl *a* dimer, 18025-08-6; BChl *a*, 17499-98-8; Chl *a*, 479-61-8.

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Discrimination of Rotational Isomeric States in Cycloalkanes by Solid-State CP-MAS ^{13}C NMR Spectroscopy†

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Abstract: The solid-state behavior of three cycloalkanes, cyclododecane, cyclotetraeicosane, and cyclohexatriacontane, was investigated by means of temperature-dependent magic angle cross-polarization ^{13}C NMR experiments. For the two smaller ring molecules a state of high internal mobility like the "rotator phase" in *n*-alkanes was detected. It could be correlated with a phase transition in the solid state visible by means of DSC. In the case of $(CH_2)_{12}$ this is 151 K below the melting point, and in the case of $(CH_2)_{24}$ it is 25 K below the melting transition. The CP-MAS ^{13}C NMR spectra show a transition from the fast exchange to the slow exchange regime of magnetically nonequivalent states. By comparison with X-ray diffraction data the well-resolved resonance signals for the low-temperature phases were assigned to molecular segments distinguished by the rotational isomeric states of the carbon-carbon bonds. Chemical shift differences due to conformational isomerism were as large as 12 ppm; thus, they exceed "packing effects" by far.

Recently cycloalkanes found rising interest as an appropriate model system to investigate specific defect structures in poly(ethylene) crystals. Studies on cycloalkanes were reported using infrared spectroscopy, X-ray diffraction, and the longitudinal acoustic modes, measured by Raman spectroscopy. Some interesting details were reported about the thermal behavior of cycloalkanes. Several of the ring alkanes undergo one or more phase transitions in the solid state. Some of those show a greater heat and also a greater entropy of transition than does the melting transition.[1-7]

^{13}C NMR spectroscopy has been reported as a potentially useful tool for the observation of rotational isomeric states in aliphatic chain molecules.[8-13] However, often the high exchange rates of

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the conformational sites in solution do not allow the resolution of different signals for the different conformers. This is not the case for high-resolution ^{13}C NMR spectra obtained with the cross-polarization[14] and the magic angle spinning technique[15] of molecules in the crystalline or in the glassy state. The resonance signals of these spectra appear at isotropic chemical shift positions like liquid-state NMR signals, although solid-state and liquid-state isotropic chemical shifts may not coincide.[16]

Because of the restricted internal mobility of the molecules in the solid state, nuclei at different conformational sites but indentical in other respects can give different signals. Recently we reported CP-MAS ^{13}C NMR investigations on ditactic poly(1,2-dimethyltetramethylenes).[17-19] Chemical shifts varied up to 8 ppm for carbon atoms distinguished by their conformational states only.

It is well established that *n*-alkanes crystallize in an all-anti (trans) conformation. Besides the end group signals their CP-MAS ^{13}C NMR spectra show only one signal. In cycloalkanes a certain number of carbon–carbon bonds are constrained to gauche conformations because of the ring structure. Hence, cycloalkanes are excellent models for the investigation of shift effects in $(CH_2)_n$ chain molecules which arise from conformational isomerism. On the other hand, CP-MAS ^{13}C NMR spectra can be a useful instrument to obtain further knowledge about the solid-state behavior of these systems.

Anet et al. reported solution ^{13}C NMR spectra of cyclododecane, cyclotetradecane, and cyclohexadecane. By cooling down the solutions to −130 and −150 °C they have been able to obtain slow exchange spectra concerning the conformational interconversion.[20-22] CP-MAS ^{13}C NMR spectra of a cycloalkane were first reported by our group on cyclotetraeicosane.[23] Experiments were restricted to room temperature. Only one signal could be resolved. This indicated a high internal mobility of the ring molecule in the solid state. At room temperature the time-averaged surrounding is the same for all carbon atoms. Hence, at least one phase transition in the solid state had to be expected. This was confirmed by independent studies of other groups and ours.[6,7]

The present study was directed toward these problems by temperature-dependent CP-MAS ^{13}C NMR studies on cyclododecane ($(CH_2)_{12}$), cyclotetraeicosane ($(CH_2)_{24}$), and cyclohexatriacontane ($(CH_2)_{36}$).

Experimental Section

Cyclododecane was prepared by hydrogenation of cyclododecene (Aldrich) in cyclohexane at 70 °C under a H_2 pressure of 7 bar with a palladium catalyst (5% on $CaCO_3$, Stream Chemicals). The catalyst was removed by filtration afterwards, and the solvent was evaporated. The raw crystalline product was purified twice by sublimation at 10^{-4} torr.

Cyclotetraeicosane and cyclohexatriacontane were prepared by metathesis reaction of cyclododecene. Cyclododecene (0.1 mol) boiled over potassium for several hours and distilled under reduced pressure (112 °C, 15 torr) was dissolved in 1 L of cyclohexane under argon. After addition of 2×10^{-4} mol of C_2H_5OH the polymerization was initiated by simultaneous injection of 2×10^{-4} mol of WCl_6 and 8×10^{-4} mol of $C_2H_5AlCl_2$ in solution.

After 1 h the solution was filtered and the solvent was removed under reduced pressure. The residue was treated with a cyclohexane/isopropyl alcohol mixture (20:80 by volume) to dissolve the oligomers. After removal of the solvent mixture 3 g of the oligomers was dissolved in 10 mL of THF and separated by preparative GPC. Two 2-m long columns, one with a diameter of 4 cm and the other with a diameter of 2.5 cm, were filled with Merckogel OR-PVA 6000, particle size 36–45 μm. THF was used as eluting solvent. A differential refractometer and a fraction collector were applied. The separation was repeated up to five times. Samples were freeze-dried and then subjected to hydrogenation as described for cyclododecane. The raw crystalline products were purified by recrystallization from cyclohexane/acetone.

Thermal Investigations. Melting points and solid-state phase transitions were determined by means of a Perkin-Elmer DSC-2 differential scanning calorimeter with a heating rate of 2.5 deg/min.

^{13}C NMR spectra were recorded on a Bruker CXP 300 spectrometer at 75.47 Hz. For the solution-state spectra of $(CH_2)_{12}$ propane-d_1 was used as a solvent. NMR stabilization was obtained by locking to the ^2H signal of monodeuteriopropane. Me_4Si was used for the reference peak.

Solid-state ^{13}C NMR spectra were obtained by using the MAS technique. If not indicated otherwise the spin locking cross-polarization technique was employed to generate ^{13}C observation. Cross-polarization time was usually 3 ms followed by the ^{13}C observation period during which the proton decoupling field was maintained. The repeating time for the pulse experiment was 30 s. Chemical shifts were determined by using the signal of the crystalline fraction of linear poly(ethylene) as the reference peak. For this purpose all MAS ^{13}C NMR spectra reported in this paper were determined additionally from cycloalkane samples to which a pellet of poly(ethylene) had been added. The chemical shift of the crystalline poly(ethylene) was set to 33.63 ppm compared to Me_4Si. This is according to the data published by Earl and VanderHart.[24] Hence, assuming that the signal of the crystalline poly(ethylene) phase does not change with temperature, the chemical shifts refer to Me_4Si. The rotor was spun by dry nitrogen gas, which was cooled by means of liquid nitrogen with a home-built heat exchange apparatus. Temperature control was achieved by a heating element installed inside the transfer tube for the nitrogen and a thermo couple installed aside the spinning rotor.

Results and Discussion

Cyclodecane. In the left of Figure 1 the solution spectra of cyclododecane are shown at various temperatures (see also Anet et al.[20]). The spectrum at 220 K exhibits one sharp signal. All carbon nuclei are equivalent with respect to the NMR time scale. When the temperature is lowered we observed a broadening of the signal and finally at 150 K two sharp resonances with an intensity ratio of 1:2. Obviously at low temperatures the carbon atoms occupy two nonequivalent sites. The exchange rate is slow with respect to the NMR time scale. The coalescence temperature of the transition from the slow exchange to the fast exchange regime was determined between 175 and 190 K.

There is no reason to assume any specific interaction between cyclododecane and the solvent propane. Hence, the NMR spectra have to be explained by the exchange of the carbon atoms between two conformational sites.

The spectra in the right of Figure 1 were obtained in the solid state with the MAS-CP technique. Although the melting point of cyclododecane is 333.4 K[1] we observed one sharp signal at 298 K. This indicates that also in the crystalline state the molecules have a high internal mobility. On an average all carbon atoms are found in all conformational sites. When the temperature is lowered the signal broadens, and finally at 155 K two well-resolved signals with an intensity ratio of about 1:2 can be detected. Solid-state spectra obtained by high-power decoupling MAS techniques without cross-polarization could only be obtained above 190 K, where the cyclododecane gave one signal. At lower temperatures T_1 relaxation times of the carbons were too long to obtain sufficiently high signal intensities. This too indicates the internal mobility of the molecules in the crystalline state between 190 K and the melting transition. The similarity of the solution and the

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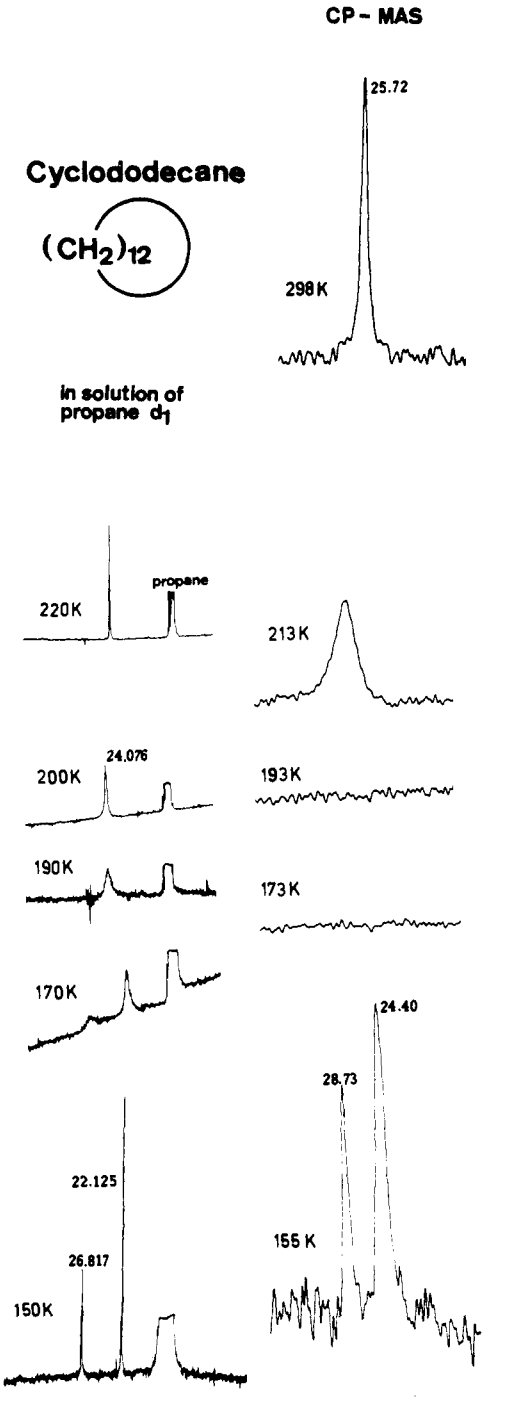

Figure 1. Liquid-state and solid-state CP-MAS ^{13}C NMR spectra of cyclododecane at various temperatures.

solid-state spectra is evident. The chemical shift difference between the two slow exchange resonance signals is 4.69 ppm in solution and 4.33 ppm in the solid state. The discrepancy is small compared to the effect itself. Hence, we conclude that the solid-state spectra show the same slow-exchange–fast-exchange transition of two conformational sites as the solution spectra.

From X-ray diffraction data obtained by Dunitz et al.[25,26] it is known that at room temperature the atoms of cyclododecane have a high thermal mobility. The conformation was determined as shown in Figure 2.[25] The molecule has an approximate D_4 symmetry. Bond angles are tetrahedral and carbon–carbon bond lengths are about 1.54 Å. The numbers at the molecular model drawn in Figure 2 give the rotational angles of the carbon–carbon

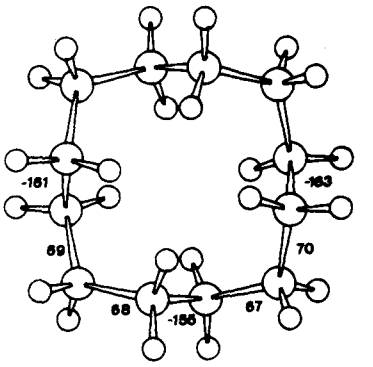

Figure 2. Conformational model of cyclododecane from X-ray diffraction data (ref 26).

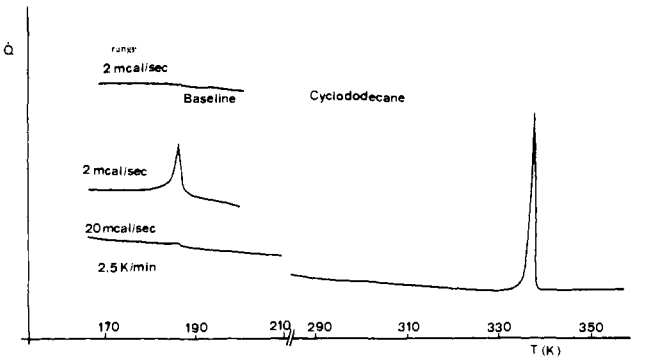

Figure 3. DSC trace of cyclododecane.

bonds. Two enantiomeric forms of this conformation have to be considered: $(g^+ag^+)_4$ and $(g^-ag^-)_4$, where $g^+ = 60°$, $g^- = -60°$, and $a = 180°$.

At room temperature the X-ray diffraction patterns are in agreement with a statitical distribution of the enantiomers. Hence, the conformation of a molecule at a certain place in the crystal lattice is independent of the conformations of the surrounding molecules. The X-ray diffraction data indicate a solid-state phase transition between 170 and 190 K. Dunitz et al. gave the following explantion: In the high-temperature phase the molecules still can change from one enantiomeric form to the other. In the low-temperature phase they do not have the freedom for this inversion.

Figure 3 shows the thermal behavior of cyclododecane from differential scanning calorimetric measurements. Besides the melting transition at 333.4 K we detected a second phase transition at 184.4 K. This second phase transition occurs within the experimental limits at the coalescence temperature of the ^{13}C NMR experiments in solution as well as in the solid state. Cyclododecane behaves similary to *n*-alkanes. In the pseudohexagonal (rotator) phase the latter are also characterized by a high internal mobility.[27] The difference of 151 K between the melting temperature and the solid-state phase transition is extremely large. The ^{13}C NMR spectra show that in the solid state the molecules behave very much like in solution. In the "pseudorotator phase"[28] the internal mobility of the molecule leads to a similar freedom of conformational interconversion as in solution. On average all carbon atoms occupy both conformational sites with the same probabilities. In the low-temperature phase the molecules adopt the same conformation as detected in the slow-exchange regime of the solution spectra. We conclude that the solid-state phase transition can be explained by the temperature dependence of the conformational exchange rate.

Averaging the slow-exchange shifts weighed by their intensities results in the fast-exchange resonance in the case of the solid-state spectra. In agreement with the X-ray diffraction data this shows that in both phases the molecules adopt the same two enantiomeric

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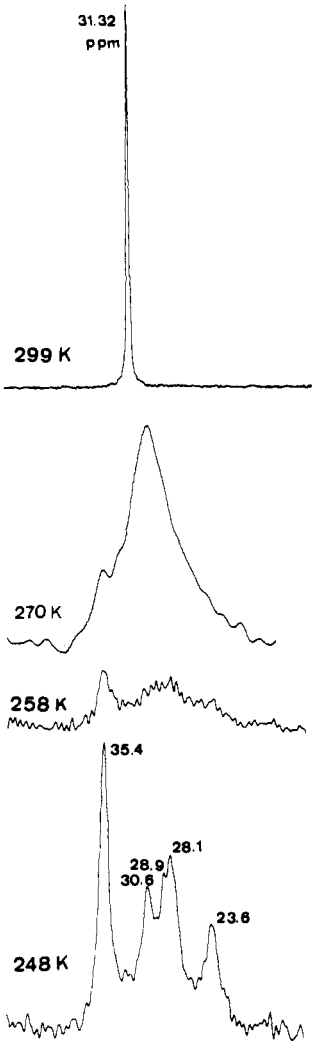

Figure 4. Solid-state CP-MAS ^{13}C NMR spectra of cyclotetraeicosane at various temperatures.

ring conformations. For the solution spectra the fast-exchange chemical shift cannot be calculated in the same way. The signal measured at 200 K is shifted 0.38 ppm upfield compared to the average from the slow-exchange spectrum. The reason therefore might be the temperature dependence of the reference signal itself (Me_4Si in propane).[29]

Although it does not affect our discussion, we have to mention that the chemical shifts determined in solution against Me_4Si differ by about 2 ppm from those in the solid state. This is in the range of solvent effects and similar to shift differences between solid-state and liquid-state spectra as reported by Lippmaa.[16]

As the conformational state of the molecules was known from X-ray diffraction measurements, an unambiguous assignment of the signals in the slow-exchange regime of the ^{13}C NMR spectra is possible. The picture of the molecular model in Figure 2 shows two different conformational sites of the carbon atoms: Four carbons in the corners of the molecule are within the center of an *agga* sequence, the eight carbons inbetween are within a *gagg* sequence. This is in agreement with a twofold splitting of the signal with an intensity ratio of 1:2. Hence, the signal at 28.73/26.82 ppm has to be assigned to the carbons within the *agga* sequences, and the signal at 24.40/22.13 is due to carbon atoms in the center of *gagg* segments.

Cyclotetraeicosane. Figure 4 shows the solid-state CP-MAS ^{13}C NMR spectra of cyclotetraeicosane, the 24-membered ring, at various temperatures. It was not possible to measure liquid-state spectra of this compound at temperatures low enough to reach the slow-exchange regime of the conformational interconversion. The solubility in ethane or propane was too poor.

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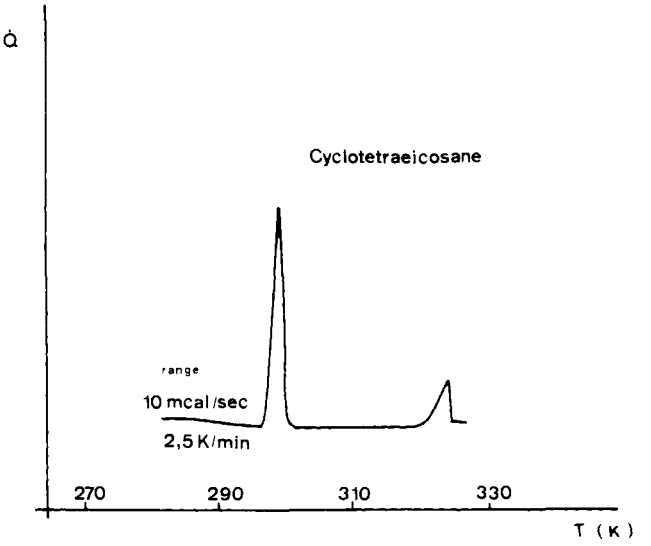


Figure 5. DSC trace of cyclotetraeicosane.

In the solid state we found a single resonance signal at room temperature. Lowering the temperature resulted in a splitting into five well-resolved signals. The coalescence temperature is between 293 and 297 K. Figure 5 shows the DSC diagram of $(CH_2)_{24}$. As for cyclododecane we found a second phase transition. At 297 K it is 25 K below the melting point at 322 K.

As in the case of cyclodecane the slow-to-fast-exchange transition in the NMR spectra is correlated with a solid-state phase transition which is clearly reflected by the thermal behavior. The ^{13}C NMR spectra show the high internal mobility in the high-temperature phase, while in the low-temperature phase five different conformational sites are discriminated. Hence, it is the freedom of the conformational interconversion of the molecules which is the reason for the solid-state phase transition.

While the DSC diagrams show a much bigger heat of transition for the melting process as for the solid-state phase transition for cyclododecane, the opposite is the case for cyclotetraeicosane. In addition the coalescence temperature of the fast-to-slow-exchange transition is much higher for the 24-membered ring. This indicates the slower kinetics of the interconversion. The pseudorotator phase transition of cyclotetraeicosane is only 25 K below the melting point compared to 151 K in case of cyclododecane. This reflects in total that the conformational interconversion for the larger ring is much more complex. The energy difference between the two phases is bigger for $(CH_2)_{24}$ than for the smaller ring and also the processes involved have a higher energy of activation.

The conformation of $(CH_2)_{24}$ was investigated by X-ray diffraction techniques at 113 K.[3] A drawing of one enantiomeric form of the resulting molecular model is shown in Figure 6. The numbers at the bonds indicate the rotational angles as determined by X-ray diffraction techniques. Two parallel all-anti strands are bridged by two *ggagg* loops. This results in an approximate C_2 symmetry. The molecule is not free of strain. The rotational angles deviate slightly from the ideal staggered angles in a diamond lattice. The largest deviations occur in the chain bridges with 17° and 14°.

The slow-exchange ^{13}C NMR spectrum has to be explained by the conformation shown. If we take into account only the different isomeric states of the bonds in α- and β-position on both sides of the observed carbon, we have to consider five conformational sequences within the molecule. Eight carbon atoms are in the center of an *aaaa* segment. Four carbons at a time are in the center of an *agga*, *aagg*, *gagg*, and an *aaag* segment. The five different conformational segments can explain the spectrum with its five signals. The ratio of the population of the carbon atoms in an identical surrounding is 2:1:1:1:1, which is in agreement with the intensity ratio of the signals.

Table I. ^{13}C NMR Shifts of Cycloalkanes Relative to $(CH_3)_4Si$

conform. sites	$(CH_2)_{36}$[a,d]	$(CH_2)_{24}$[a,d]	$(CH_2)_{16}$[b,c]	$(CH_2)_{14}$[b,c]	$(CH_2)_{12}$[a,d]	$(CH_2)_{12}$[b,d]	$(CH_2)_{12}$[b,c]
ga·gg	23.8/23.6	23.6		21.3	24.4	22.1	21.8
ga·ag			22.8	23.3			
gg·aa	27.6	28.1	26.8	26.2			
ag·ga	28.5	28.9	27.0	26.8	28.7	26.8	26.6
ga·aa	30.2	30.6					
aa·aa	35.5	35.4					

[a] Solid state. [b] In solution. [c] Data from ref 20 and 21. [d] Data from this work.

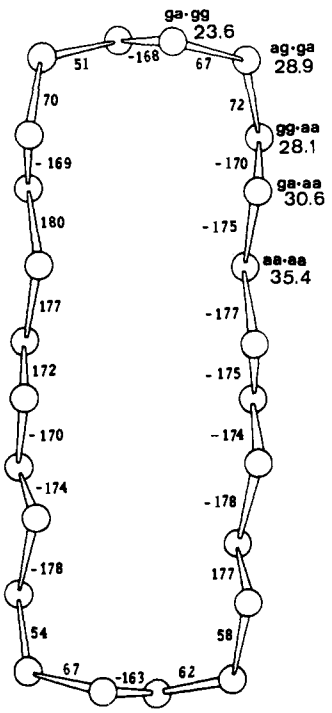


Figure 6. Conformational model of cyclotetraeicosane from X-ray diffraction data (ref 3).

In the literature conformational shift effects are explained in most cases by the so-called γ-gauche effect.[8-10] Comparison of the spectrum and the molecular model in Figure 6 shows that the resonances cannot be explained solely by γ-gauche interactions. We have to consider that the conformation of an α-bond influences the chemical shift, although the rotational isomerism of the α-bonds does not alter the position of the observed nucleus relative to the α-, β-, and γ-carbon atoms. However, the influence of the α-bond isomerism is in agreement with the slow exchange spectra of 2,3-dimethylbutane, 1,2-dimethylcyclohexane, and other analogous compounds in solution.[30,31] Figure 7 shows the fast exchange and the slow exchange spectrum of 2,3-dimethylbutane in a solution of propane-d_1. In the fast exchange regime two signals are detected, one for the CH_3 carbon atoms and one for the CH carbons. In the slow exchange regime the CH signal splits up into two resonances and the CH_3 signal splits up into three resonances. The splitting of the CH_3 signal has to be explained by the γ-gauche effect. The same explanation does not hold for the occurrence of two CH signals in the slow exchange spectrum. No carbon atoms are in the position γ to the CH groups. While in the anti state of the CH–CH bond the vicinal CH_3 groups are in gauche and anti positions to each other, two CH_3 groups are in gauche and anti positions to their γ-carbons and two CH_3 groups are in gauche$^+$ and gauche$^-$ positions to their γ-carbons in the gauche conformation of the CH–CH bond. This results in an upfield shift of 2.7 ppm for the CH ^{13}C NMR signal in CH–CH gauche conformers compared to the CH signal in the corresponding anti conformer. Hence, it is clearly shown that not only

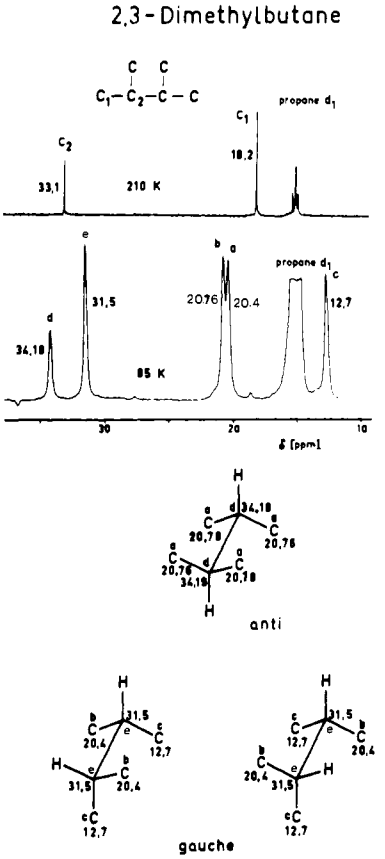
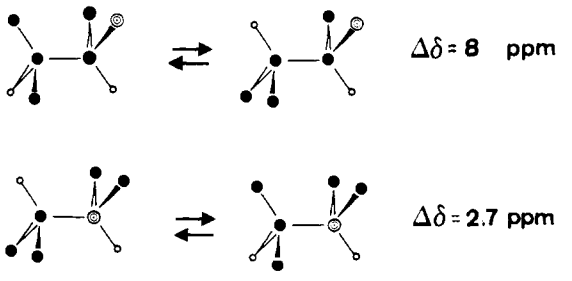


Figure 7. ^{13}C NMR solution spectra of 2,3-dimethylbutane in the fast- and slow-exchange regime of the CH–CH bond rotation.

Scheme I



the positions of γ-carbon atoms induce conformational shift effects. Additionally the position of the adjacent carbon atoms relative to each other determines the chemical shift of a ^{13}C NMR signal, as shown in Scheme I.

It is conclusive with this observation when we found five signals in the low-temperature MAS ^{13}C NMR spectrum of cyclotetraeicosane. They must be assigned to the five conformational sequences within the molecule in the crystalline state with regard to the α- and β-bonds on each side of a certain CH_2 group. The most intense and most downfield signal at 35.4 ppm belongs to the *aaaa* segments. The comparison with the cyclododecane spectra shows that the most upfield signal at 23.6 ppm is that of the *gagg* segments, and one of the signals at 28.1 and 28.9 ppm belongs to the *agga* segments.

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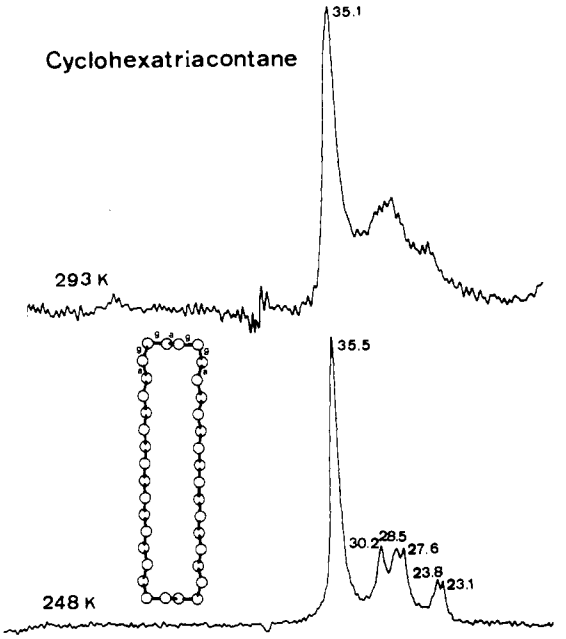

Figure 8. Solid-state CP-MAS ^{13}C NMR spectra of cyclohexatriacontane with the conformational model from X-ray diffraction (ref 4).

For a complete assignment we want to compare our data with the slow-exchange chemical shifts determined for cyclododecane, cyclotetradecane, and cyclohexadecane in solution by Anet et al. Table I shows the chemical shifts relative to Me_4Si and the assignments from ref 20 and 21 in comparison with those from Figures 1, 4, and 8. The small divergence of the chemical shifts of dissolved cyclododecane can be explained by the different solvents and temperatures. Compared to the solution we could detect an upfield shift of 1.6 and 2.1 ppm for the slow exchange signals of cyclododecane in the solid. It is reasonable to consider a similar difference for the comparison of the solid-state $(CH_2)_{24}$ spectrum with the solution spectra of $(CH_2)_{14}$ and $(CH_2)_{16}$. The splitting patterns are then very similar. The spectra of cyclotetradecane and cyclohexadecane both show signals for *agga* and *ggaa* segments; in addition, a signal for the *gagg* segments is resolved in the spectrum of $(CH_2)_{14}$. Chemical shift differences between those signals are about the same as those of the corresponding signals in the $(CH_2)_{24}$ spectrum, if we assign the signals at 28.1 and 28.9 ppm to the *agga* and the *ggaa* sites. Hence, the signal at 30.6 ppm belongs to the *aaag* sements. An assignment of the 28.1-ppm signal to the *ggaa* sites and the 28.9-ppm signal to the *agga* sites is in accordance with the $(CH_2)_{16}$ spectrum. Because of the small difference of the signals it is not certain and can be reversed. Regarding the other signals the scheme appears to be consistent, although we have to consider shifts due to packing effects.

Cyclohexatriacontane. The MAS ^{13}C NMR spectra of cyclohexatriacontane ($(CH_2)_{36}$) are shown in Figure 8 at 293 and 248 K. The crystal structure and conformation of the ring molecule were investigated before by X-ray diffraction techniques.[4] As in the case of the other rings the lattice is monoclinic. The crystal conformation is similar to the one of cyclotetraeicosane and is shown in Figure 6. The planar all-anti conformation of the straight segments is distorted to a small extent which was shown by LAM measurements.[4] Because of the equivalence of the crystal conformation, the MAS ^{13}C NMR spectrum in the slow-exchange regime is very much the same as that of $(CH_2)_{24}$. While the *aaaa* signal of cyclotetraeicosane is twice as intense as the four other signals, in the spectrum of cyclohexatriaconatane it has to be five times as intense as the *aaag*, *agga*, *ggaa*, and *gagg* signals. Figure 8 shows that this is the case. The intensity ratios are in agreement with the expected 5:1:1:1:1 ratio. However, the most upfield shifted signal which we assigned to the *gagg* segments splits into two signals. The difference is small, and we think the doublet still has to be assigned to the carbons in the center of a *gagg* sequence. Small differences in the rotational angles of the loops or "packing effects" might be responsible for the splitting.

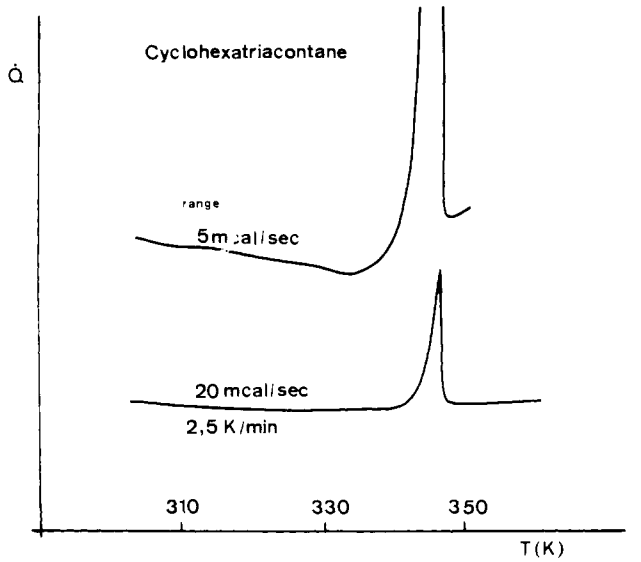

Figure 9. DSC trace of cycohexatriacontane.

While the CP-MAS ^{13}C NMR spectra of cyclododecane and cyclotetraeicosane clearly proved the high internal mobility of the ring molecules in the high-temperature phase, we could not find any evidence for a "pseudorotator phase" for cyclohexatriacontane. Agreement here with the DSC trace shown in Figure 9 does not indicate any other phase transition beside the melting transition. We conclude that for large ring molecules like $(CH_2)_{36}$ the molecular packing does not allow conformational interconversion like for the smaller rings.

Conclusions

The example of the ring alkanes shows that CP-MAS ^{13}C NMR experiments can give detailed information about the conformational structure and dynamics of a molecule. We want to point out several aspects of the data discussed above. In the case of the smaller rings the CP-MAS ^{13}C NMR spectra demonstrate the internal mobility in the pseudorotator phase very obviously. However, the fact that the spectra show resolved signals of different conformations for the low-temperature solid state does not mean that the molecules do not undergo conformational changes at all. Motions which are either very slow or very fast with respect to the NMR time scale cannot be detected by our experiments. In addition it is in common to all three compounds that we could obtain the well-resolved spectra only at temperatures significantly below the coalescence temperature of the solid-state phase transition. This means that we have to consider conformational exchange processes in the low-temperature solid-state phases too, although they are considerably slower and of a different kind as compared with the fast-exchange regime.

In the high-temperature phases all carbon atoms occupy all conformational sites in the time average with equal probability. Although in the case of $(CH_2)_{24}$ the conformation of the high-temperature phase is not necessarily identical with the one in the low-temperature phase, this seems remarkable. We can only think of two explanations: (1) The molecules rearrange themselves indepenently of adjacent molecules. All segments can adopt all conformations independently of their orientation and of the packing in the lattice. (2) The space and mobility of a molecule are restricted, and only space-filling conformations are allowed. In this case the molecules have to move around their center like a bicycle chain around the two sprockets. Otherwise we would not be able to detect a sharp averaged signal.

As the mobility decreases with increasing chain length, and we could not detect a "pseudorotator phase" for cyclohexatriacontane, the first explanation seems more reasonable. However, if option 2 described the system, then the lack of a transition in cyclo-

hexatriacontane could be due to packing energies associated with the parallel linear chains.

We explained the splitting in the slow-exchange spectra by the magnetic nonequivalence which results from frozen conformations. In addition molecular packing variations may cause chemical shift differences by modifying bond angles, by the orientation of sources of anisotropic magnetic susceptibility, or by short-range interactions with the carbon orbitals. The splitting of the cyclododecane signal in solution differs by only 0.35 ppm from that in the solid state. Most probably this difference is due to the molecular packing in the crystal, but it is also negligibly small compared to the conformational effects. The chemical shift differences in the slow exchange regime of cycloalkanes are as big as 12 ppm. The influence of the rotational isomerism exceeds the so-called packing effects by far. Therefore, it seems reasonable to discuss the cycloalkane spectra to a first approximation solely in terms of conformational inequivalence. The situation becomes more complicated when ring molecules are compared to linear molecules. We found a shift difference of 1.8 ppm between the *aaaa* signal of the cycloalkanes and the signal of the all-anti segments in crystalline poly(ethylene).

VanderHart discussed chemical shift differences of CP-MAS ^{13}C NMR signals of *n*-alkanes with respet to molecular packing.[33] He determined a downfield shift of 1.3 ppm for the signal of the internal CH_2 carbons in triclinic C-20 compared to orthorhombic C-23.

The chemical shift of the *aaaa* segments in the cycloalkanes is closer to that of the internal CH_2 carbons in the triclinic C-20 than to the shift of the carbons of poly(ethylene) or the other *n*-alkanes. This difference of the isotropic chemical shifts may result from the variation of the chain geometries or from some crystal packing variations. Certainly there is a difference between the all-anti segments in the constrained ring molecules compared to the all-anti segments in poly(ethylene), but there is no evidence for a similar difference between *n*-alkanes like C-20 and C-23.

VanderHart explained the discrepancy of 1.3 ppm for the *n*-alkanes by variations in the molecular packing. Probably the same explanation holds at least partially for the 1.8 ppm difference of the cycloalkanes and poly(ethylene). Hence, our data also show that the effect could be due to changes in the geometry of the chain.

Fast-exchange spectra of aliphatic chain molecules, especially of poly(propylene), have been interpreted with respect to the conformational characteristics.[8-10,34,35] Calculations based solely on a γ-gauche effect of -5 to -5.5 ppm yielded chemical shifts and distributions of the conformational states in good agreement with the spectra and the RIS model.[36] The ring spectra and the spectrum of 2,3-dimethylbutane in the slow-exchange regime which we report here give γ-gauche effects varying from -4.8 to -8 ppm, if we neglect all other conformational variations. In addition, the spectra clearly show that changes of the isomeric rotational states of the two bonds in the position α to the observed carbon atom can yield an effect as big as -5 ppm. Also, the effects we discussed are not additive. Obviously variations which do not affect the arrangement of the carbons in γ-position are averaged in the fast exchange regime of conformational interconversions to a high extent. Thus, the treatment solely in terms of γ-gauche interactions becomes possible. Nevertheless we think great care has to be taken for the interpretation of fast-exchange spectra with γ-gauche increments which were not determined from spectra of compounds with analogous structure.

In the introduction we mentioned that cycloalkanes might serve as an appropriate model system for the investigation of conformational characteristics of the amorphous phase and specific crystal defect structures in poly(ethylene). For linear poly(ethylene) the MAS-CP ^{13}C NMR spectrum gives a sharp signal for the crystalline phase and a broad resonance shifted upfield by about 1.8 ppm for the amorphous regions.[13] In the folds as well as in the amorphous phases conformational segments should exist which are similar to those in the cycloalkane folds. Therefore, we should expect a splitting to a similar extent as for the cycloalkanes. Yet even at very low temperatures it has not been possible to observe signals of frozen conformations of poly(ethylene) different from the all-anti chains in the crystals. We do not understand so far why poly(ethylene) behaves in a different way. The reasons have to be discussed in terms of an unusual mobility in the poly(ethylene) chains, strain within the chains in the amorphous regions, and the different types of folds in poly(ethylene) crystals. Further investigations with regard to these questions are under way.

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Registry No. Cyclododecane, 294-62-2; cyclotetraeicosane, 297-03-0; cyclohexatriacontane, 297-50-7; cyclododecene, 1501-82-2.

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